

Impact of fixation/drying conditions on fixation rate, leachability and bioefficacy in CCA-C treated red pine and southern pine

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Abstract: Red pine (*Pinus resinosa* Ait) and southern pine (*Pinus* spp.) sapwood blocks were pressure treated with CCA-C at retention of 6.4, 2.0, 1.5 kg·m⁻³ followed by fixation using 11 post-treatment schedules ranging from 50-70 °C and 5 different relative humidity conditions. The effect of these post-treatment schedules on fixation rate, chemical leachability and decay resistant once were evaluated to better understand the effects of fixation/drying conditions on leachability and biodeterioration. Southern pine blocks fixes slightly slower than red pine. Fixation of CCA at high temperature high humidity, essential initially fixation at high humidity for fixation/drying schedules, resulted in lower leaching of chromium and arsenic elements than high temperature low humidity or initially fixation at the high temperature low humidity conditions. Copper leaching was indicated no significant difference under 11 fixation/drying conditions for both species. Weight losses for southern pine by *Chaetomium globosum* was lower than red pine by *Gloeophyllum trabeum*. There were some different capacities of decay resistance for both species under those post treatment conditions.

Key words: Red pine; Southern pine; Bioefficacy; Leachability; Fixation rate; CCA-C; Temperature; Humidity

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Introduction

The chemistry and physics of waterborne CCA wood preservatives fixation reaction in wood have been extensively studied (Chou *et al.* 1973; Cooper *et al.* 1993; Kaldas & Cooper 1996; Preston & Mckaig 1983). There seems to be general agreement that when hexavalent Chromium is no longer detectable and has primarily been reduced to chromium (Cr⁺⁶) complete reduction of the chromium indicates that the potential for copper and arsenic has been minimized (Avramidis & Ruddick 1989; Chen *et al.* 1994). This is of concern for long-term bioefficacy, especially when CCA preservative retention levels are set nearer minimum fungal-toxic thresholds, it has also become a health concern that can include issues such as ground water contamination, soil contamination, or direct skin contact with unfixed CCA preservative, so reducing CCA leaching from treated wood has long been a goal because chemical reactions between components of the treating solution and constituents of the wood are not completely understood (Boone & Winandy 1995). In order to minimize leaching, fixation between the preservative and the wood must be

completed.

Many researchers have reported that the use of elevated temperature and relative humidity can interfere with fixation or effect leachability to chromated copper arsenic preservative treated wood (Cooper *et al.* 1997; Lee *et al.* 1993; Lebow *et al.* 1996; Ung & Cooper 1996.). Conradie and Pizzi (1987) showed that the of CCA leachate increased with an increase in drying temperature generally an increase of more than four times, from 25 to 120 °C (Conradie & Pizzi 1987). Alexander and Cooper (1993) found that rate of CCA fixation in wood was highly temperature dependant with relative humidity or wet bulb temperature playing an important role in the process and the relative humidity effect could be explained by its effect on the surface temperature of approaching the wet bulb temperature of the surrounding under during drying condition. In addition, Ung and Cooper (1996) showed that rate of fixation was slowed substantially as a result of cooling of the wood surface under the drying condition. However, as long as the wood moisture content did not drop below the fiber saturation point, any adverse effects on CCA leaching from the fixed wood did not appear.

Peek and Willeitner (1998) and Preston and Mckaig (1983) have shown that wood fixed at high temperatures resists decay as well or better than wood fixed at ambient conditions. Gray (1990) looked at the effect of solution temperature at time of treatment (5 to 35 °C) and found no difference in resistance to brown-rot fungus. Kartal (1999) observed

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there was no significant effect in the biological resistance among fixation temperatures used.

Although high temperature and high relative humidity can accelerate the fixation reaction to CCA treated wood, this requires large energy amounts and therefore increases the cost of post treatment, and also in-service leachability of CCA is related to the temperature and MC the wood fixation (Lee *et al* 1993). Especially, dry-bulb temperature limits have to consider meet the condition of concerns for loss of strength (Boone & Winandy 1995). However, the possible need for wet-bulb temperature limits and the adequacy of currently used redrying schedule to meet these considerations are of some concern.

This objective of this study is to examine the effects of the fixation drying condition on fixation performance, leachability and decay resistant are for CCA-C treated red pine (*Pinus resinosa* Ait) and southern pine (*Pinus* spp).

Material and method

All samples of CCA-C treated red pine and southern pine from the first study (Guo & Cooper 1999) were cleaned for leaching test and Decay test.

After the fixation times in the post treatment condition were achieved, each Fixation condition six 19-mm cub blocks were cut from the samples of 19 mm x 19 mm x 300 mm sub 3 for red pine and 19 mm x 19 mm x 250 mm sub 3 for southern pine. Those blocks were subjected to AWP A E11-97 standard

leaching test, and repeat the test (America Wood Preservation Association 1997). The amounts of copper, chromium and arsenic from CCA treated blocks were determined by atomic absorption spectroscopic (AAS) analyses of the leachates collected from the 2 weeks cycle. Percentage loss of copper, chromium and arsenic elements was determined from the cumulative amount (μg) of each element in the leachate and total amount added to the blocks during CCA treatment.

Following fixation and leaching test, each fixation condition six 19-mm cub blocks before and after decay were placed in a condition chamber at 40 °C and 68% RH to 12% MC. Tests for decay resistance were run following AWP A E 10-91 (American Wood Preservation Association 1991). A soft-rot fungus (*Chaetomium globosum*) was selected for southern pine, and a brown-rot fungus (*Gloeophyllum trabeum*) was selected for red pine at both low retentions. The duration of the test was performed for 12 weeks. Weight loss by decay as a percent of original weight was determined for each block and those values were used in ANOVA calculation.

Results and discussion

Target retention for both red pine and southern pine was 1.5, 2.0 and 6.4 kg m^{-3} . For calculated retention levels of these samples of 11 post treatment groups based on weight gain are shown in Table 1.

Table 1. Summary of actual retention and time to 99.9% fixation for red pine (R.P) and southern pine (S.P)

Sched ule No	Wood Species	Actual Reten- tion / $\text{kg}\cdot\text{m}^{-3}$	Time to 99.9% Fixation /h	Actual Retention kg/m^3	Time to 99.9% Fixation /h	Actual Retention kg/m^3	Time to 99.9 % Fixation /h
Target	Retention	6.4		2.0		1.5	
1	R.P	7.1	7.5	2.2	6.0	1.6	5.0
	S.P	7.4	8.8	2.4	6.5	1.5	5.5
2	R.P	7.2	7.5	2.2	6.0	1.6	5.0
	S.P	7.2	7.5	2.4	6.5	1.9	6.0
3	R.P	7.5	8.0	1.9	5.5	1.8	5.5
	S.P	6.8	7.5	2.4	6.5	1.9	6.0
4	R.P	6.8	7.5	2.1	5.8	1.6	5.5
	S.P	6.8	8.0	1.9	6.0	1.5	5.5
5	R.P	6.4	6.5	2.1	5.8	1.3	5.0
	S.P	7.2	8.0	1.9	6.0	1.6	6.0
6	R.P	7.4	7.7	2.3	6.0	1.7	5.5
	S.P	6.7	7.0	2.2	6.0	1.9	6.0
7	R.P	6.7	18.2	2.3	14.0	1.7	13.0
	S.P	6.4	22.8	2.4	16.0	1.8	15.0
8	R.P	6.2	11.0	1.9	9.0	1.6	8.0
	S.P	6.8	14.5	2.2	10.0	1.6	9.0
9	R.P	6.7	7.0	2.3	5.5	1.7	4.5
	S.P	7.0	8.0	2.2	5.5	1.7	5.0
10	R.P	6.9	3.5	2.1	2.5	1.6	2.5
	S.P	7.0	4.0	2.9	2.5	1.7	2.0
11	R.P	6.5	8.5	2.0	6.0	1.5	5.0
	S.P	7.7	10.0	2.4	6.5	1.9	6.0

The time is estimated for 99.9% fixation of chromium (Cr^{+6}). Southern pine usually had slight longer average fixation time than red pine. Longest fixation time in the study was 22.8 h for southern pine and 18.2 h for red pine at 50/38 °C, shortest fixation time had only 4.0 h for southern pine and 3.5 h for red pine at 70/68 °C. There was slight variation in fixation time under 6 fixation/drying schedule (schedules 1-6), ranging from 6.5 to 8.0 h for red pine, from 7.0 to 8.8

h southern pine.

The study results confirm that there were difference in leaching of chromium, and arsenic losses among 6 combine fixation/drying schedules (schedule 1-6), and also same result were reflected in schedules 7-11 for both red pine and southern pine. Fig. 1, 2, 3 and 4 shows the average percentage of chemical elements leached of two repeated leaching tests from two species and 11 post fixation schedules.

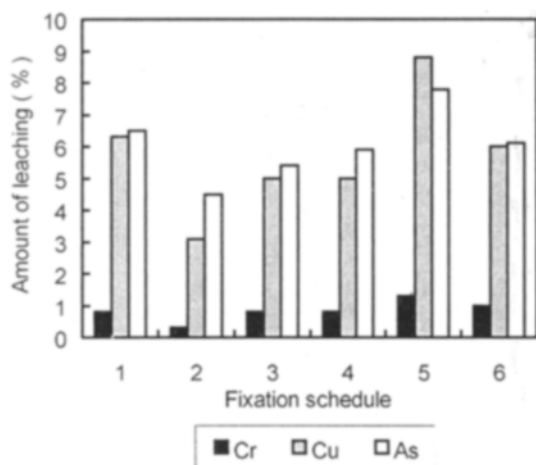


Fig. 1 Average leaching loss of CCA under schedules 1-6 for red pine

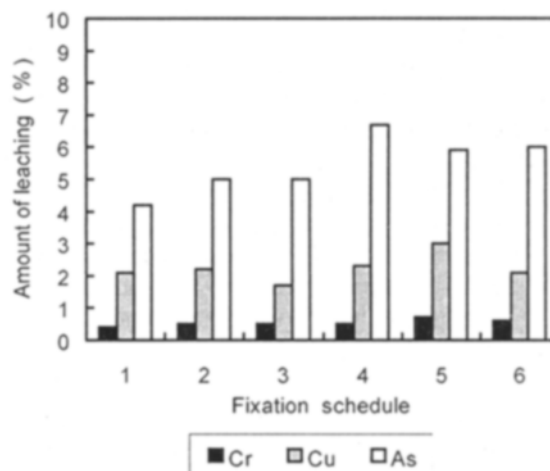


Fig. 2 Average leaching loss of CCA under schedules 1-6 for southern pine

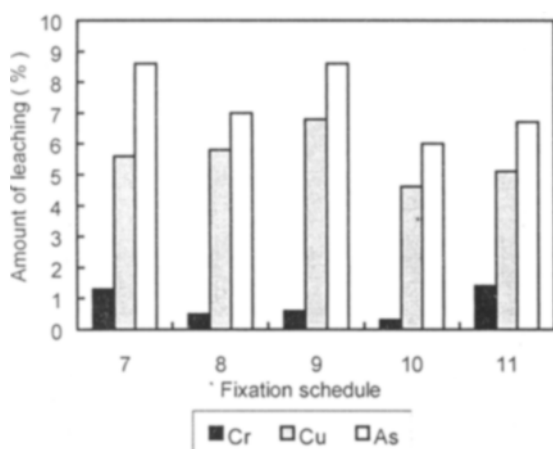


Fig. 3 Average leaching loss of CCA Under schedules 7-11 for red pine

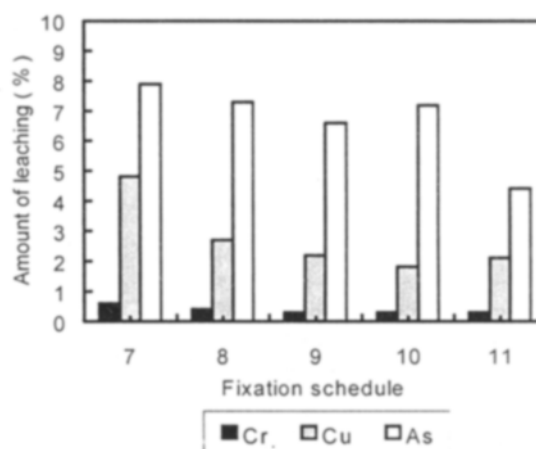


Fig. 4 Average leaching loss of CCA under schedules 7-11 for southern pine

Chromium was the most stable of the three elements with leaching from 0.3%-1.4% of the total absorbed in wood during the treatment. For combine fixation/drying schedules (schedule 1-6), schedule 1, 2, 3 due to adopt initially fixation at 50/49 °C then sequence elevating temperature and dropping relative humidity, comparatively low chromium leaching losses in the condition were observed from 0.3% to

0.8%. The least amount of chromium leaching occurred in initially fixation at schedule 1-2 (0.4% for S.P, 0.3% for R.P), and the most leaching of chromium occurred in schedule 5 (1.3% for R.P, 0.7% for S.P). Comparatively low arsenic leaching losses were also observed for both red pine and southern pine blocks in the combine schedule 1, 2, and 3. Arsenic losses ranged between 4.5%-7.8% for R.P and 4.2%-6.7%

for S.P. The least amount leaching of arsenic occurred in schedule 2 (4.5 for R.P) and schedule 1 (4.2% for S.P), and the highest arsenic leaching losses occurred in schedule 6 (7.8% for R.P) and schedule 4 (6.7% for S.P). For copper, although the least amount of leaching occurred in schedule 3 for southern pine and schedule 2 for red pine, the test analysis indicated there is no significant difference for 6 combine fixation/drying schedules (Fig. 1, 2).

The leaching of chromium and arsenic elements at schedule 4-5 were comparative high leaching losses because initially and middle fixation at high temperature low humidity conditions. This condition caused fast evaporation of water and MCs reducing rapid to go fiber saturation point or drop out FSP. So it could result in low MC interferes with mobility of the CCA components, and unreacted CCA components deposited in the cell lumens earlier in spite of finally fixation at high temperature high humidity adopted.

The same significant trend is apparent in the leaching of chromium and arsenic to schedules 7-11. We observed that there were low leaching losses of all three elements from red pine and southern pine at high temperature high relative humidity conditions (schedule 8, 10), comparing the result with fixation at high temperature low relative humidity (schedule 7, 9, 11). Low chromium losses from CCA treated both species blocks at 50/49 °C and 70/68 °C were 0.3 to 0.5% for red pine and 0.3 to 0.4 for southern pine. Slightly lower arsenic leaching losses were determined at 50/49°C (7.0% for red pine, 7.3 % for southern pine) and 70/68 °C (6.0% for R.P) than at 50/38 °C (8.8% for R.P, 7.9% for S.P) and 70/50 °C (8.6% for R.P).

Amount of copper losses was between 4.6%-6.8% for R.P and 1.8%-4.8% for S.P at schedules 7-11, but there was also no significant difference for effecting of fixation conditions.

Fig. 5, 6, 7, 8 showed the relationship between fixation/drying conditions, retention and weight loss for southern pine by soft-rot fungus and red pine by blown-rot fungus under 11 schedules. In the untreated control blocks, the average weight loss was 39.97% for S.P by *C. globosum* and 38.41% for R.P by *G. trabeum*. It is clear from weight loss observed that there is always a direct effect of retention on weight losses. With actual retention increased, weight loss was reduced under the same fixation/drying condition. Weight loss of red pine by *G. trabeum* was lower than southern pine by *C. globosum*. For example, the average weight loss of all samples at 11 schedules in the same target retention were 7.55g (ret: 2.0 kg·m⁻³) and 10.21g (ret 1.5 kg·m⁻³) for R.P, 6.40g (ret: 2.0 kg·m⁻³) and 9.16g (ret: 1.5 kg·m⁻³) for S.P

Comparison of the effect of different fixation/drying

conditions on weight loss, Table 2 showed that there were different for both two species at schedule 1-6. Weight losses of the blocks at schedule 1-3 were slight lower than those at schedule 4-6. For schedule 7-11 less weight loss of both species at high temperature high humidity (schedule 8, 10) were achieved at the same target retention.

In order to determine the effects of the fixation/drying conditions, retention on weight loss, statistical analysis of variance (Table 3, 4) showed that both were significant, and the effects of humidity on weight loss were also significant (Table 5, 6), whereas there was no significant effect of temperature on weight loss.

Table 2. Average weight lose for southern pine and red pine by decay test

Run No:	Weight lose by <i>C.gboleum</i> /g		Weight lose (g) by <i>G.trabeum</i> /g	
	Southern pine		Red pine	
	Ret: 1.5 kg · m ⁻³	Ret:2.0 kg · m ⁻³	Ret: 1.5 kg · m ⁻³	Ret:2.0 kg · m ⁻³
1	10.54	7.18	9.15	5.81
2	8.74	6.04	8.38	6.25
3	9.32	7.76	7.65	5.88
4	11.77	8.86	9.41	6.40
5	11.04	8.58	12.92	6.88
6	10.52	8.21	11.42	6.71
7	10.63	7.59	8.94	6.87
8	9.27	6.84	7.96	6.01
9	11.47	8.18	9.37	6.25
10	9.66	5.80	8.03	6.24
11	9.38	8.03	7.53	7.16

Conclusions

These results confirm that fixation/drying conditions affect fixation rate, leaching and decay resistance. As temperature and humidity during fixation are increased up 50-70 °C and 95 %, a more leach and decay resistant products are formed than the temperature at lower humidity. Generally, conditions that resulted in initially fixed at high temperature low humidity produced higher chromium and arsenic leaching losses. Maintaining smallest wet-bulb depression in fixation course, essential initially fix, reduced leaching of chromium and arsenic for both species. Almost all elements leaching was lower southern pine than red pine under 11 fixation drying conditions.

It was noted that there was no significant effect in the decay resistance between 50-70 °C despite the fact that relative humidity played a substantial role. Initial fixation at high temperature high humidity could improve CCA solution to diffuse rapid into wood cell walls, and resist wood-rot fungi effectively.

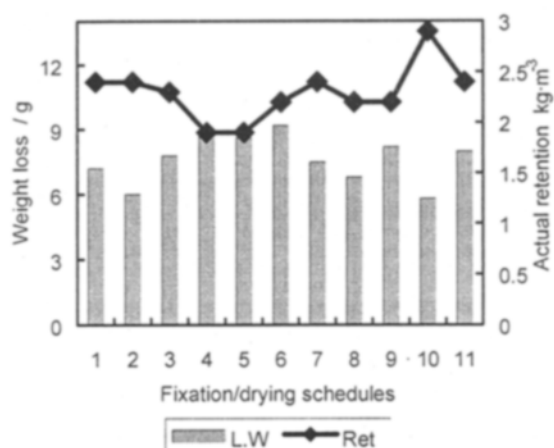


Fig. 5 Relationship between fixation/drying schedule, retention and weight loss for southern pine (the target retention = 2.0 kg/m^3) by *G. globosum*

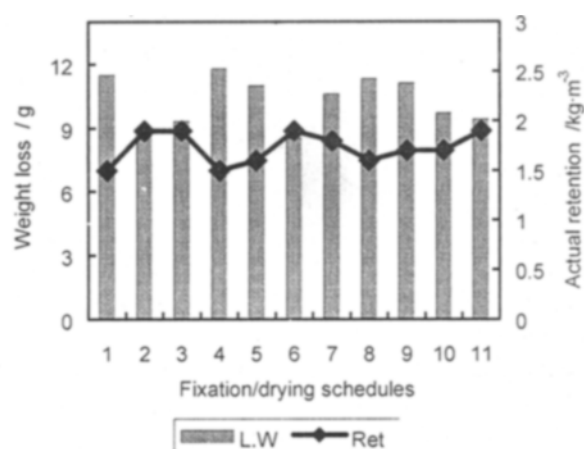


Fig. 6 Relationship between fixation/drying schedule, retention and weight loss for southern pine (the target retention = 1.5 kg/m^3) by *G. globosum*

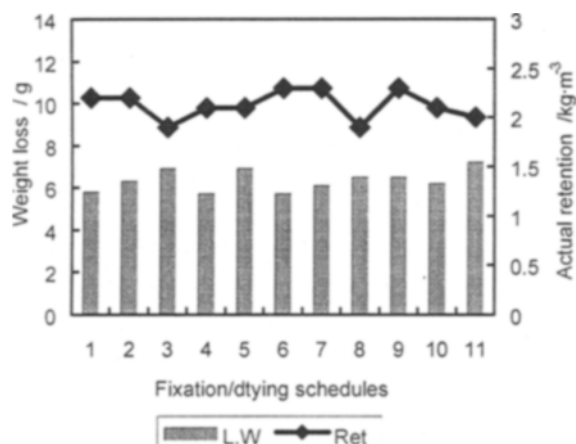


Fig. 7 Relationship between fixation/drying schedule, retention and weight loss for red pine (the target retention = 2.0 kg/m^3) by *G. thabeum*

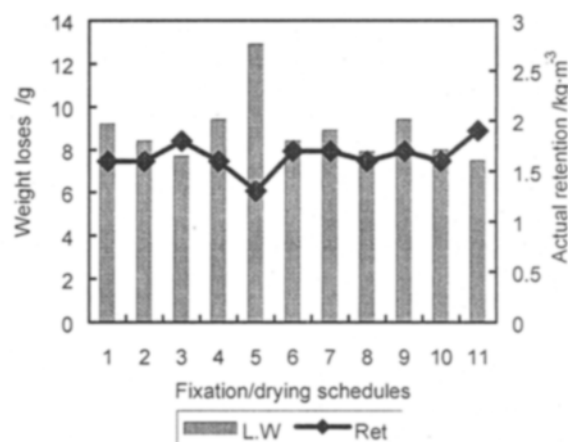


Fig. 8 Relationship between fixation/drying schedule, retention and weight loss for red pine (the target retention = 1.5 kg/m^3) by *G. thabeum*

Table 3. Analysis of variance procedure of relationship between weight losses and schedule, actual retention for southern pine by *C. globosum* at schedule 1-6 (target retention = $2.0, 1.5 \text{ kg/m}^3$)

ce of Vari	SS	df	MS	F	Pr > F
Schedule	64.6543792	5	12.9308758	1.76	0.1342
Retention	188.80130	5	37.760261	5.15	0.0005
Interaction	0.0000000	1	0.0000000	0.00	1.0000

Table 4. Analysis of variance procedure of relationship between weight losses and schedule, actual retention for red pine by *G. trabeum* at schedule 1-6 (target retention = $2.0, 1.5 \text{ kg/m}^3$)

ce of Vari	SS	df	MS	F	Pr > F
Schedule	67.324450	5	13.4648900	4.38	0.0018
Retention	269.26846	7	38.466923	12.52	<0.0001
Interaction	0.000000	-1	0.0000000	0.00	<0.0001

Table 5. Analysis of variance procedure of relationship between weight losses and temperature, humidity, retention for southern pine by *C. globosum* at schedule 7-11 (target retention = 2.0, 1.5 kg/m³)

ce of Vari	SS	df	MS	F	Pr > F
Temperature	4.387145000	2	2.19357250	0.79	0.4650
Relative Humidity	23.060353	4	5.7605883	2.08	0.1143
Retention	17.119270	2	8.5596350	3.08	0.0635

Table 6. Analysis of variance procedure of relationship between weight losses and temperature, humidity, retention for red pine by *G.traebeam* at schedule 7-11b (retention = 2.0, 1.5 kg/m³)

ce of Vari	SS	df	MS	F	Pr > F
Temperature	0.04445250	2	0.22226250	0.1	0.9865
Relative Humidity	25.271223	4	6.3178053	3.87	0.0082
Retention	48.046065	5	9.6092130	5.88	0.0002

References

- Alexanater, D.L., Ung, T.Y. and Cooper, P. A.1993. Effects of temperature and humidity on CCA-C fixation in pine samples [J]. Wood Production, **2**(2): 29-45.
- American Wood Preservers' Association. 1997. Standard method of determining the leaching of wood preservatives [M]. The AWWPA Book of Standards, AWWPA, Woodstock, MD.
- American Wood Preservers' Association. 1991. Standard method of testing wood preservatives by laboratory soil-block cultures [M]. The AWWPA Book of Standards, AWWPA, Woodstock, MD.
- Avramidis, S. and Ruddick, J.N.R. 1989. Effect of temperature and moisture on CCA fixation. Holz-als , Roh-und Werksott, **7**(8): 328.
- Boone, R.S. and Winandy, J.E. 1995. Effects of redying schedules on preservative fixation and strength of CCA-treated lumber. Forest prod. J., **45**(9): 65-73.
- Chen, J.M., Kaldas, M., Ung, T.U., and Cooper, A.P. 1994. Heat transfer and wood moisture effects in moderate temperature fixation of CCA treated wood [R]. IRG/WP/40022, stockholm, Sweet, 13pp.
- Chou, C.K., Chandler, J.A. and Preston, R.D. 1973. Micro-distribution of metal elements in wood impregnated with a copper-chrome-arsenic preservative as determined by analytical electron microscopy. Wood Sci. Technol., **7**: 151-160.
- Conradie, W.E. and Pizzi, A. 1987. Progressive heat inactivation of CCA biological performance. Proc. Amer. Wood Preserves' Assoc. **83**: 32-49.
- Cooper, P.A., Alexander, D.L. and Ung, T.Y. 1993. What is chemical fixation? [C] In: chromium-containing waterborne wood preservatives, fixation and environmental issues. Forest Prod. J. Madison, Wis, pp 7-13.
- Cooper, P. A. and Ung, T.Y. 1993. A simple quantitative measure of CCA fixation [J]. Forest Prod. J., **43**(5): 19-20.
- Cooper, P.A., Ung, T.Y., and Kamden, D.P., 1997. Fixation and leaching of red maple treated with CCA-C [J]. Forest Prod. J. **47**(2): 70-74.
- Gray, S.M. 1990. The effect of treatment temperature on the biological performance of CCA-treated wood [R]. Document No IRG/WP/3624.
- Guo, A.L; Cooper, P.A. 1999. Effect of post Treatment temperature and humidity conditions on fixation performance of CCA-C treated red pine and southern pine [J]. Journal of forestry research, **10**(3): 141-146.
- Lee, A.W.C., Grafton, J.C., and Tainter, F.H. 1993. Effect of rapid redrying shortly after treatment on leachability of CCA-treated southern pine [J]. Forest Prod. J., **43**(2): 37-40.
- Lebow, S.T., Morrell, J.J., and Milota, M.R. 1996. Western wood species treated with chromium copper arsenic: Effect of moisture content [J]. Forest Prod. J., **46**(2): 68-70.
- M. Kaldas, and Cooper, P.A. 1996. Effect of wood moisture content on rate of fixation and leachability of CCA-treated red pine [J]. Forest Prod. J., **46**(10): 67-71.
- Peek, R. and Willeitner, H. 1988. Fundamentals on steam fixation of chromated wood preservatives [R]. Documents No IRG/WP/3483.
- Preston, A., and J. Mckaig. 1983. Effect of accelerated fixation in decay of CCA-treated wood [J]. Forest Prod. J., **33**(11): 41-44.
- Kartal, S.N. 1999. The leachability, biological resistant and mechanical properties of wood treated with CCA and CCB preservatives [R]. IRG /WP/99-30207
- Ung, T.Y. and Cooper, P.A. 1996. Feasibility of drying CCA-treated red pine pole during fixation [J]. Forest Prod. J., **46**(6): 46-50.